

**PART I**

**OFFICE OF NAVAL RESEARCH**

**END-OF-THE-YEAR REPORT**

**PUBLICATIONS / PATENTS / PRESENTATIONS / HONORS /  
STUDENTS REPORT**

**for**

**GRANT NUMBER: N00014-94-C-10706**



**R & T CODE: 3134067**

**CHEMICAL REACTIVITY STUDIES OF HIGH TEMPERATURE  
SUPERCONDUCTOR STRUCTURES AND DEVICES**

**JOHN T. MCDEVITT**

**THE UNIVERSITY OF TEXAS AT AUSTIN**

**DEPARTMENT OF CHEMISTRY & BIOCHEMISTRY  
WELCH 4.428  
AUSTIN, TX 78712-1167**

**MAY 31, 1995**

**Reproduction in whole, or in part, is permitted for any purpose of the  
United States Government.**

**This document has been approved for public release and sale, its  
distribution is unlimited.**

**DTIC QUALITY INSPECTED 3**

**19950601 021**

**OFFICE OF NAVAL RESEARCH  
PUBLICATIONS / PATENTS / PRESENTATIONS / HONORS REPORT**

**R&T Number: 3134067**

**Contract/Grant Number: N00014-94-C-10706**

**Contract/Grant Title: Chemical Reactivity Studies of High Temperature  
Superconductor Structures and Devices**

**Principal Investigator: John T. McDevitt**

**Mailing Address: Dept. of Chemistry & Biochemistry, The University of  
Texas at Austin, Austin, TX 78712-1167**

**Phone Number: (512) 471-0046      Fax Number: (512) 471-8696**

**E-mail Address: mcdevitt@huckel.cm.utexas.edu**

**WWW Homepage: <http://huckel.cm.utexas.edu/cejones/mcdevitt.html>**

- A.    Number of papers submitted to refereed journals, but not published  
(below listed): 5**
- B. + Number of papers published in refereed journals (below listed): 2**
- C. + Number of books or chapters submitted, but not yet published: 0**
- D. + Number of books or chapters published : 0**
- E. + Number of printed technical reports/non-refereed papers: 0**
- F.    Number of patents filed (below listed): 2**
- G. + Number of patents granted : 0**
- H. + Number of invited presentations (below listed): 13**
- I. + Number of submitted presentations (below listed): 2**
- J. + Honors/Awards/Prizes for contract/grant employees (below listed): 2**
- K.    Total number of Full-time equivalent Graduate Students and Post-  
Doctoral associates supported during this period, under this R&T  
project number (below listed): 2**
- Graduate Students: 0**
- Post-Doctoral Associates: 2**
- Female Graduate Students: 0**
- Female Post-Doctoral Associates: 0**
- Minority\* Graduate Students: 0**
- Minority\* Post-Doctoral Associates: 0**
- Asian Graduate Students: 0**
- Asian Post-Doctoral Associates: 2**
- L. + Other funding (below listed): 5**

Accession For	
NTIS    CRA&I	<input checked="checked" type="checkbox"/>
DTIC    TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification _____	
By _____	
Distribution / _____	
Availability Codes	
Dist	Avail and/or Special
A-1	

#### **A. PAPERS SUBMITTED TO REFEREED JOURNALS**

5. J.P. Zhou, J.-S. Zhou, J.B. Goodenough and J.T. McDevitt, "Physical and Chemical Properties of  $(Y_{1-x}Ca_x)(Ba_{2-x}La_x)Cu_3O_{7-\delta}$ ", J. of Supercon. **1995**, 8, , in press.
4. John T. McDevitt, Rung-Kuang Lo, Ji-Ping Zhou, Steven G. Haupt, Jianai Zhao, and David C. Jurbergs, Kaimen Chen and Chad A. Mirkin, "Molecular Level Control Over the Interfacial Properties of High-Tc Superconductors", Science, submitted.
3. Ji-Ping Zhou, Joel J. Kampa, Mark Arendt, David R. Riley, K. Bussmann, Richard J. Lagow and John T. McDevitt, "Corrosion Resistant  $YBa_2Cu_3O_{7-x}$  Materials by Light Surface Fluorination," Physica C, submitted.
2. Kaimin Chen, Chad A. Mirkin, Rung-Kuang Lo, Jianai Zhao, and John T. McDevitt, "Surveying the Surface Coordination Chemistry of a Superconductor: Spontaneous Adsorption of Monolayer Films of Redox-active Ligands on  $YBa_2Cu_3O_{7-\delta}$ ", J. Am. Chem. Soc., accepted.
1. Ji-Ping Zhou, Steven M. Savoy, Rung-Kuang Lo, Jianai Zhao, Mark Arendt, Y.T. Zhu, A. Manthiram and John T. McDevitt, "Improved Corrosion Resistance of Cation Substituted  $YBa_2Cu_3O_{7-\delta}$ ," Appl. Phys. Lett., accepted.

#### **B. PAPERS PUBLISHED IN REFEREED JOURNALS**

2. Ji-Ping Zhou, David R. Riley, Y.T. Zhu, A. Manthiram and John T. McDevitt, "Chemically Tailored Corrosion Resistant High-Tc Phases," J. Am. Chem. Soc., **1994**, 116, 9389-9390.
1. J.S. Zhou, J.P. Zhou, J.T. McDevitt, and J.B. Goodenough, "Chain Contribution to the Seebeck Coefficient in  $YBa_2Cu_3O_{7-\delta}$ ," Phys. Rev. B, **1995**, 51, 3250-3253.

#### **F. PATENT APPLICATIONS**

2. "New Methods for Fabrication of Superconductor Devices, Anti-Corrosion Layers, and Adhesion Layers", University of Texas at Austin & Northwestern University, Patent Filed, May 22, 1995.
1. "Chemically Tailored Corrosion Resistant High-Tc Superconductor Thin Film Structures and Devices," University of Texas at Austin, Patent Filed, October 6, 1994.

## **LICENSING AGREEMENTS**

1. "Chemically Tailored Corrosion Resistant High-Tc Superconductor Thin Film Structures and Devices," University of Texas at Austin, Agreement Executed with Superconductive Components, Inc. on April 25, 1995.

## **CONFIDENTIALITY AGREEMENTS**

4. "New Methods for Fabrication of Superconductor Devices, Anti-Corrosion Layers, and Adhesion Layers", " University of Texas at Austin & Northwestern University, Agreement Executed with Quantum Magnetics Corporation on April 13, 1995.
3. "New Methods for Fabrication of Superconductor Devices, Anti-Corrosion Layers, and Adhesion Layers", " University of Texas at Austin & Northwestern University, Agreement Executed with Intermagnetics General Corporation on May 15, 1995.
2. "Chemically Tailored Corrosion Resistant High-Tc Superconductor Thin Film Structures and Devices," University of Texas at Austin, Agreement Executed with Intermagnetics General Corporation on July 8, 1994.
1. "Chemically Tailored Corrosion Resistant High-Tc Superconductor Thin Film Structures and Devices," University of Texas at Austin, Agreement Executed with Conductus Corporation on June 10, 1994.

## **H. INVITED PRESENTATIONS**

13. "Molecule and Crystal Engineering of High Temperature Superconductor Structures and Devices," IBM Yorktown Heights Research Facility, April 13, 1995.
12. "Molecule-Superconductor Structures and Devices," Southwest Regional American Chemical Society Meeting, Fort Worth, TX, November 13-16, 1994.
11. "Conductive Polymer Coated High-Tc Devices," Advanced Laboratory Exposition and Conference," San Jose, CA, October 25-27, 1994.
10. "Conductive Polymer/High-Tc Superconductor Sandwich Structures: An Example of a Molecular Switch for Controlling Superconductivity," Federation of Analytical Chemistry and Spectroscopy Society Meeting, St. Louis, MO, October 4, 1994.
9. "Charge-Transfer Reactions at Conductive Polymer/Superconductor Interfaces Measured at Temperatures Above and Below Tc," Federation of Analytical Chemistry and Spectroscopy Society Meeting, St. Louis, MO, October 4, 1994.

8. "Chemistry of Superconductor Materials," Naval Research Laboratory, Washington, D.C., August 26, 1994.
7. "Fabrication and Study of Molecule/Superconductor Structures and Devices," American Chemical Society Meeting, Microstructure at Electrode Surfaces Symposium, Washington, DC, August 24, 1994.
6. "Hybrid Molecule/Superconductor Structures and Devices," Inorganic Gordon Research Conference, Wolfeboro, NH, July 31-August 5, 1994.
5. "Conductive Polymer/High-Tc Superconductor Bilayer Structures and Devices," International Conference on Science and Technology of Synthetic Metals, Seoul, Korea, July 24-29, 1994.
4. "Conductive Polymer Switch for Controlling Superconductivity," 35th IUPAC International Symposium on Macromolecules, Akron, OH, July 17, 1994.
3. "Hybrid Molecule/Superconductor Structures and Devices," Institut für Anorganische Chemie, University of Aachen, Aachen, Germany, June 17, 1994.
2. "Molecule-Superconductor Assemblies and Devices," 6th International Fischer Symposium on Nanotechniques in Electrochemistry, University of Karlsruhe, Germany, Plenary Lecture, June 15, 1994.
1. "Chemistry of High Temperature Superconductors," Conductus, Inc., Sunnyvale, CA, May 27, 1994.

#### **I. PRESENTATIONS**

2. "Conductive Polymer/Superconductor Bilayer Structures," American Chemical Society Meeting, Division of Physical Chemistry, Washington, DC, August 24, 1994 (poster session).
1. "Chemically Tailored Corrosion Resistant High-Tc Phases," Inorganic Gordon Conference, Wolfeboro, NH, August 1-2, 1994 (poster session).

#### **J. HONORS / AWARDS / NEWS ARTICLES**

2. During the last year Dr. John T. McDevitt was promoted from the level of Assistant Professor to that of Associate Professor.
1. In recognition of the significance and importance of research completed in Dr. McDevitt's laboratory under the ONR contract, the article listed below was published:

"Superconductor Tailored for Greater Stability" Chemical & Engineering News, October 31, 1994, page 17.

## **K. PERSONNEL**

Dr. Jianai Zhao and Dr. Ji-Ping Zhou were supported during the last year by this ONR contract.

## **L. OTHER CURRENT RESEARCH SUPPORT**

5. National Science Foundation. "Superconductor-Based Electron Transfer Studies Below T<sub>c</sub>." \$269,000; 1/1/93 to 12/31/95. (grant renewal award). No overlap with the ONR grant.
4. National Science Foundation. "Presidential Young Investigator". \$125,000 (base) plus \$375,000 (matching funds); 9/1/90 to 8/31/95. No overlap with the ONR grant.
3. National Science Foundation & Office of Naval Research Joint Grant. "Thin Film Deposition Equipment Grant." \$45,626. 4/15/95 to 4/14/96. ONR and NSF cooperated for the purchase of this equipment that is used extensively for research which is relevant to both agencies.
2. Texas Advanced Technology Program. "Fabrication and Study of Hybrid Molecule-Superconductor Structures and Devices". \$146,300; 1/1/94 to 12/31/95. No overlap with the ONR grant.
1. The Welch Foundation. "Electrochemical Investigations of High Temperature Superconductors". \$91,500; 6/1/93 to 5/31/96. No overlap with the ONR grant.

## **PART II**

**A. Principal Investigator: John T. McDevitt**

**B. Current Telephone Number: (512) 471-0046**

**C. Cognizant ONR Scientific Officer: Dr. John C. Pazik**

**D. Brief Description of Project (100-200 words) :**

During the past, year we have initiated detailed studies of the mechanism of the corrosion of the technologically important superconductor,  $\text{YBa}_2\text{Cu}_3\text{O}_7$ . From these studies, we have identified lattice stress and strain as an important factor which influences the corrosion rate of this compound. This important clue to the reactivity problem remained unidentified in the prior 300 papers that had been published in the area. Armed with this information, we initiated crystal engineering studies through which we optimize the lattice by alloying elements such as  $\text{Ca}^{2+}$  into the  $\text{Y}^{3+}$  site and  $\text{La}^{3+}$  into the  $\text{Ba}^{2+}$  site. Here we found that the corrosion resistance increases with increasing  $y$  in  $\text{Y}_{1-y}\text{Ca}_y\text{Ba}_{2-y}\text{La}_y\text{Cu}_3\text{O}_7$ . The chemical degradation behavior in water for both bulk and thin film samples of  $\text{Y}_{1-y}\text{Ca}_y\text{Ba}_{2-y}\text{La}_y\text{Cu}_3\text{O}_7$  has been studied along with similar data for the unsubstituted compound,  $\text{YBa}_2\text{Cu}_3\text{O}_7$ . The composition of  $\text{Y}_{0.6}\text{Ca}_{0.4}\text{Ba}_{1.6}\text{La}_{0.4}\text{Cu}_3\text{O}_{6.96}$  with a  $T_c = 80$  K was found to be at least 100 times more stable than  $\text{YBa}_2\text{Cu}_3\text{O}_{6.94}$ . The availability of these stable cuprate phases will facilitate more rapid commercialization of high- $T_c$  thin film structures and devices.

**E. Significant and Impact of Last Year's Results (100-200 words):**

Prior to our recent work, very little information was available in the literature regarding the interfacial chemical reactivity issues related to the processing and fabrication of high- $T_c$  devices. Lack of knowledge in this area has been one of the most formidable problems that has slowed progress in this technologically important area of research. The new stable materials we have identified in the past year will find utility in the preparation of more durable and better performing high- $T_c$  devices. So important are the developments in this area, that a number of high- $T_c$  start up firms, such as Conductus, Quantum Magnetix, and Intermagnetix General are in the process of evaluating our compounds and procedures for use in their commercial products. Moreover, Superconductive Components has recently licensed our technology for the preparation of bulk ceramic forms of our chemically stabilized compounds. Thus, the more rapid commercialization of high- $T_c$  superconductor devices such as Josephson junctions, SQUID's, microwave circuits, and infrared sensors will likely result from this work supported by ONR.

**F. Brief Summary of Plans for Next Year's Work (100-200 words):**

Having identified lattice stress and strain as an important factor that influences the corrosion rate of the high-T<sub>c</sub> superconductors, we will continue in the next year to explore a wide variety of chemical substitution patterns to further optimize the superconductors. Here we will strive to engineer the lattice so that both the corrosion resistance and the superconducting parameters (i.e. T<sub>c</sub> and J<sub>c</sub>) are obtained. At present, the formulation of Y<sub>0.6</sub>Ca<sub>0.4</sub>Ba<sub>1.6</sub>La<sub>0.4</sub>Cu<sub>3</sub>O<sub>6.96</sub> has been found to exhibit both excellent stability while maintaining a relatively high transition temperature of 80-82K. This formulation is an excellent candidate to serve as a protective layer for the parent compound, YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6.94</sub> which is now used extensively in the current efforts to commercialize high-T<sub>c</sub> thin film devices. Our new formulation of Y<sub>0.6</sub>Ca<sub>0.4</sub>Ba<sub>1.6</sub>La<sub>0.4</sub>Cu<sub>3</sub>O<sub>6.96</sub> is now being explored by a number of commercial firms in this context. It is our desire, however, to identify alternative stable formulations which exhibit even higher transition temperatures. Systems with T<sub>c</sub> values in excess of 85K would likely serve as good overall replacements for YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6.94</sub> in thin film applications. Therefore, over the next year we will continue our ambitious goal to search for alternative replacements for YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6.94</sub>.

**G. List of Names of Supported Post-doctorals Currently Working on the Project:**

Dr. Jianai Zhao and Dr. Ji-Ping Zhou were supported during the last year by this ONR contract.

tle change in its resistance over a period of 10 days" under these conditions.

What's interesting about this discovery, comments Francis J. DiSalvo, an inorganic chemistry professor at Cornell University, is that it "wasn't so obvious that just by fiddling a little bit with the chemistry, you could affect the corrosion resistance [so much]. ... Whether it's going to be technologically important or not depends on the applications and the engineering trade-offs."

Certainly, thin-film devices can be packaged to protect them from the environment, DiSalvo notes. Indeed, McDevitt anticipates that his substituted materials could be used as a capping layer to protect thin films of the parent compound, YBCO. And the use of a corrosion-resistant superconductor as the active layer itself could allow thin-film devices to be microfabricated more easily and with greater flexibility, McDevitt says.

McDevitt is now working with Conductus, a startup company in Sunnyvale, Calif., on the development of commercial devices that incorporate thin films of corrosion-resistant superconductors.

Ron Dagani

## Laser light employed to influence reactions

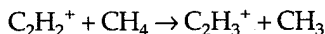
The dream of using precisely tuned laser light to control the outcome of chemical reactions moves a step closer to reality with recent findings, published by two groups working independently, that certain ion-molecule reactions are vibrational-mode selective.

Last month, Scott L. Anderson, professor of chemistry at the State University of New York, Stony Brook, and colleagues reported the surprising result that the reaction of acetylene ions with methane could be strongly influenced by excitation of the  $C_2H_2^+$  bending vibrational mode [*J. Chem. Phys.*, **101**, 5410 (1994)]. Now, chemistry professor Richard N. Zare of Stanford University and colleagues report that excitation of the "umbrella mode" vibration of the ammonium ion exerts a similar effect in the reaction of that ion with  $ND_3$  [*Science*, **266**, 259 (1994)].

Historically, efforts to direct the course of chemical reactions by using laser light have been frustrated by the fact

that vibrational coupling in most molecules quickly redistributes the energy applied to a selected vibrational mode. One exception is the water molecule, whose modes are sufficiently uncoupled to permit laser-controlled reactions, as demonstrated by University of Wisconsin chemist Fleming Crim in 1990.

The promising results of Crim's experiment led researchers to pursue reactions of more complex species. Anderson's group demonstrated that laser excitation of the bending vibrational mode of linear acetylene ions causes an enhancement by a factor of 30 in the reaction:



In contrast, excitation of the carbon-carbon stretching mode had little effect on the outcome, a surprising result because the bending vibrational mode involves a bond (the carbon-carbon bond) that is not broken during the reaction.

Anderson suggests that the change in hybridization of the carbon atoms during the reaction may explain why excitation of the bending mode gives an enhancement. "The carbon atoms must change from linear  $sp$  hybridization to  $sp^2$ , which has  $120^\circ$  bond angles," he says. "Bending motion is, therefore, just the right type of molecular motion to drive the acetylene reactant into the more reactive configuration. You could say that the bending energy goes directly into lowering the hybridization energy."

Anderson's group has examined about five different ion-molecule reactions and in each case observed mode-specific effects. But only in the case of the acetylene ion-methane reaction has such a large enhancement been observed.

In the ion-molecule reaction studied by Zare's group, ammonium ions react with  $ND_3$ . Three outcomes are possible: deuterium abstraction to form  $NH_3D^+$  and  $ND_2$ ; charge transfer to form  $NH_3$  and  $ND_3^+$ ; and proton transfer, yielding  $NH_2$  and  $ND_3H^+$ . The researchers prepared the ion reagent in two isoenergetic vibrational states of different combinations of bending and breathing motions; they found that the



*Ion-molecule reactions were studied by Zare (center) with graduate students Robert Guettler (left) and Glenn Jones.*

bending motion enhances charge transfer and deuterium abstraction and hinders proton transfer.

The umbrella bending motion of the pyramidal ammonium ion turns the molecule inside out like an umbrella in a windstorm. The breathing motion, on the other hand, stretches and contracts bonds along the N-H axes in unison. The researchers prepared the ion in two versions of about the same total energy: one version possessed 1 quantum of breathing and 2 quanta of umbrella bending, for a total internal energy of 0.63 eV; the other version had no breathing motion and 5 quanta of bending motion, for a total internal energy of 0.60 eV. Zare and colleagues note that the experiments "address directly the question of whether it is the amount of internal energy that influences the reaction outcome or if the type of the vibrational motion can also be a factor."

Finding that the reaction outcome is influenced by the bending motion of  $NH_3^+$  but is insensitive to the breathing vibration leads the researchers to conclude that this polyatomic ion-molecule reaction is indeed mode selective.

Meanwhile, efforts continue at laboratories around the country to take the concept of these experiments to the next higher level of control—developing methods that don't rely on natural vibrational modes but instead impose, by means of exquisitely controlled laser pulses, artificially created motions and outcomes.

Deborah Illman

strongly bound. It is then difficult to reverse this in a simple way."

The Israeli team has overcome this problem of strong binding between antigen and antibody by using photoisomerizable DNP spiropyran as the antigen monolayer. Irradiation of the monolayer in two steps reversibly isomerizes the spiropyran. In one photoisomeric state, the DNP spiropyran antigen recognizes the DNP antibody, but in the other state it does not.

The antigen electrode, when bound to the antibody, is irradiated with light with wavelengths of 360 to 380 nm. This converts the active DNP spiropyran antigen to an isomer that has no affinity for the DNP antibody. The antigen therefore releases the antibody, which is washed off the electrode. Subsequent irradiation of the electrode at a wavelength greater than 495 nm restores the active antigen monolayer electrode.

The immunosensor developed by Willner and colleagues is an electrochemical cell with the antigen monolayer gold electrode and an electrolyte solution containing  $K_4Fe(CN)_6$  as a redox probe. The electrochemical cell also includes a platinum secondary electrode and a Ag/AgCl reference electrode.

Interaction of the electrode with the DNP antibody results in the antibody binding to the antigen monolayer of the electrode. In this state, the electrode is insulated from the soluble redox probe and the amperometric response—the current through the device—decreases. The extent of insulation is controlled by the antibody concentration and the incubation time of the electrode with the antibody.

Following irradiation and rinsing of the electrode, a high amperometric response is obtained, indicating removal of the insulation and therefore of the antibody. Addition of the DNP antibody at this stage does not alter the response. This shows that the monolayer is inactive in this photoisomeric state. The electrode is then irradiated for a second time to restore the antigen to its active isomeric state. Addition of the DNP antibody now results in a low amperometric signal indicating insulation and therefore binding of the antibody to the electrode.

Prolonged irradiation has an adverse effect on the cyclic activity of the electrode, presumably because of partial decomposition of the antigen monolayer.

Michael Freemantle

## Superconductor tailored for greater stability

Researchers at the University of Texas, Austin, have discovered how to dramatically increase the stability of an important high-temperature superconductor, perhaps leading to its more rapid application in thin-film devices.

The cuprate superconductors that have emerged as technological contenders in the past eight years have been plagued by a tendency to degrade chemically when exposed to water, acids, and carbon dioxide. This is especially true for yttrium-barium-copper oxide ( $YBa_2Cu_3O_7$ ), which is the preferred material for thin-film applications.

The chemical literature contains some 300 papers on the chemical corrosion of high-temperature superconductors, notes John T. McDevitt, an assistant professor of chemistry at UT Austin. His own group has helped elucidate what happens when these materials are exposed to water and other reactants. And now, using what he calls "chemical detective work," McDevitt and his coworkers have found a simple solution to the problem.

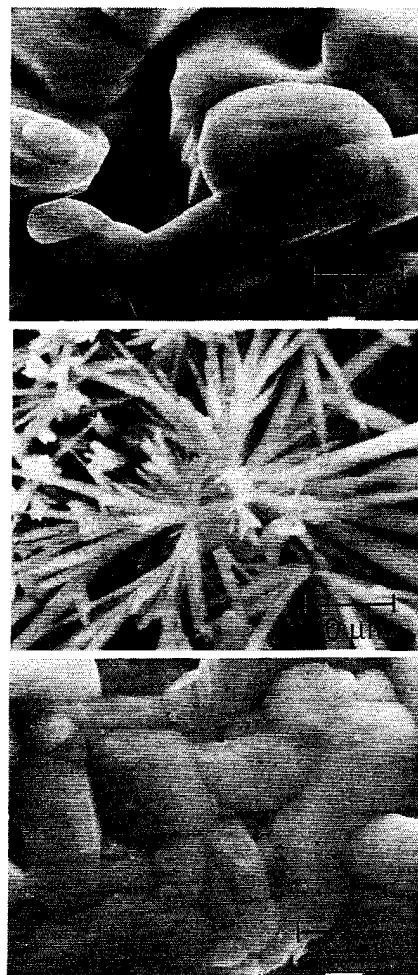
The key to making the superconductor less reactive, McDevitt explains, is to relieve the lattice strain that exists in  $YBa_2Cu_3O_7$ , which is sometimes abbreviated YBCO. This material, which becomes superconducting at about 93 K, consists of layers of yttrium cations, barium oxide, and copper oxide. Basically, McDevitt says, a mismatch of the Ba-O and some of the Cu-O bond lengths between layers can lead to internal stresses that make reaction with protons or water molecules much more favorable. Those stresses can be alleviated by making versions of YBCO that contain cationic substitutions.

McDevitt and coworkers find that substituting  $Ca^{2+}$  for about one third of the  $Y^{3+}$  and substituting  $La^{3+}$  for about one fifth of the  $Ba^{2+}$  in YBCO reduces the bond-length disparities while maintaining the "electronic bookkeeping" that is essential for preserving the superconductive properties. The resulting Y-Ca-Ba-La-Cu-O materials superconduct at slightly lower temperatures (about 10 K) than YBCO. But their corrosion resistance is increased markedly.

McDevitt and colleagues compared the reactivity of YBCO and its chemically tailored varieties by exposing them to water. As they reported a few weeks ago

[*J. Am. Chem. Soc.*, **116**, 9389 (1994)], a YBCO pellet becomes completely coated with  $BaCO_3$  crystallites (from atmospheric  $CO_2$ ) after soaking in water for two days at 25 °C, indicating significant decomposition. By contrast, Y-Ca-Ba-La-Cu-O pellets show almost no reaction after soaking in water for one month. One of the substituted materials survived more than 100 times longer than unsubstituted YBCO, the researchers note.

They also compared the reactivity of thin films of these superconductors, as grown by laser ablation. YBCO films exposed to water vapor at 75 °C degraded rapidly in the course of two hours. On the other hand, the Y-Ca-Ba-La-Cu-O film sample "showed very lit-



Scanning electron micrographs show (top) a pellet of  $YBa_2Cu_3O_{6.94}$  before corrosion, (middle) the same sample after exposure to water at 25 °C for two days, and (bottom) a pellet of corrosion-resistant  $Y_{0.6}Ca_{0.4}Ba_{1.6}La_{0.4}Cu_3O_{6.96}$  after soaking in water for 30 days.

## Chemically Tailored, Corrosion Resistant, High- $T_c$ Phases

Ji-Ping Zhou,<sup>†</sup> Steven M. Savoy,<sup>†</sup> Jianai Zhao,<sup>†</sup>  
David R. Riley,<sup>†</sup> Y. T. Zhu,<sup>†</sup> A. Manthiram,<sup>‡</sup>  
Rung-Kuang Lo,<sup>‡</sup> Damon Borich,<sup>†</sup> and John T. McDevitt<sup>\*†</sup>

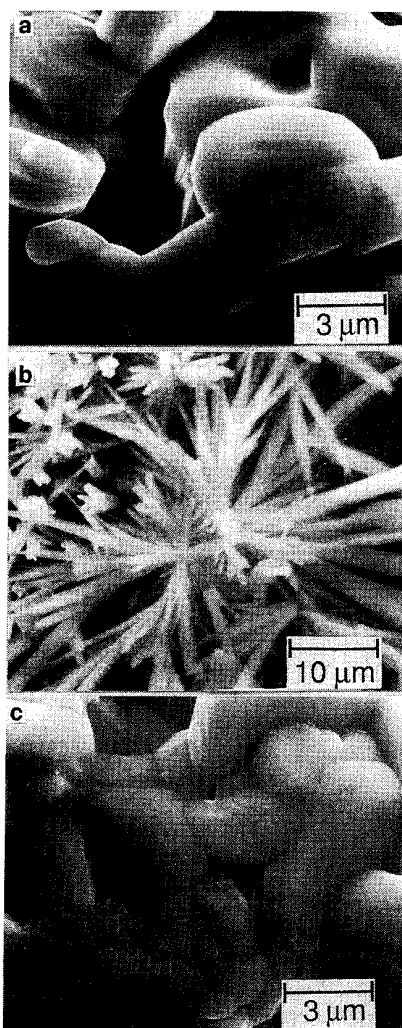
Department of Chemistry and Biochemistry and Center for  
Materials Science and Engineering  
The University of Texas at Austin  
Austin, Texas 78712

Received April 19, 1994

One of the major stumbling blocks that has plagued the practical utilization of high- $T_c$  superconductors has been the tendency of the cuprate compounds to degrade chemically when exposed to water, acids,  $\text{CO}_2$ , and  $\text{CO}$ .<sup>1-4</sup> Of the technologically important superconductors with transition temperatures above 77 K (i.e.,  $\text{YBa}_2\text{Cu}_3\text{O}_7$ ,  $\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ ,  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ , and  $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_9$ ),  $\text{YBa}_2\text{Cu}_3\text{O}_7$  is the preferred material for thin-film applications.<sup>5</sup> Unfortunately, the  $\text{YBa}_2\text{Cu}_3\text{O}_7$  compound displays the highest atmospheric corrosion reactivity of the studied cuprate materials.<sup>2</sup>

The  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  phase possesses a layered structure with a sequence along the  $c$ -axis of  $\text{Cu}(1)\text{O}_x$ - $\text{BaO}$ - $\text{Cu}(2)\text{O}_2$ - $\text{Y}$ - $\text{Cu}(2)\text{O}_2$ - $\text{BaO}$ - $\text{Cu}(1)\text{O}_x$ .<sup>6,7</sup> Any bond length mismatch between the layers can introduce internal stresses.<sup>8,9</sup> We have shown previously that samples of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  having intermediate oxygen contents corrode more slowly than samples do with either higher or lower oxygen contents.<sup>10,11</sup> This behavior cannot be explained satisfactorily along the lines of copper valence as previously hypothesized.<sup>12</sup> Rather, lattice stress appears to be an important factor which dictates the decomposition kinetics for this material.

In an effort to relieve the tensile stress and strain which exists in the  $\text{Ba-O}$  and  $\text{Cu}(2)\text{O}_2$  layers in the  $\text{YBa}_2\text{Cu}_3\text{O}_7$  structure, we have considered a number of cation substitution strategies. The  $\text{La}^{3+}$  substitution in  $\text{YBa}_{2-y}\text{La}_y\text{Cu}_3\text{O}_{7-\delta}$  causes a rapid decrease in  $T_c$  due to a disordering of oxygen in the  $\text{Cu}(1)\text{O}_x$  plane and an accompanying transfer of holes from the active  $\text{Cu}(2)\text{O}_2$  sheets to the inactive  $\text{Cu}(1)\text{O}_x$  planes.<sup>13</sup> However, it has been shown<sup>14</sup> that a cosubstitution of  $\text{Ca}^{2+}$  for  $\text{Y}^{3+}$  and  $\text{La}^{3+}$  for  $\text{Ba}^{2+}$  in the  $\text{Y}_{1-y}\text{Ca}_y\text{Ba}_{2-y}\text{La}_y\text{Cu}_3\text{O}_{7-\delta}$  system can maintain the  $T_c$  above 80 K in spite of the fact that an orthorhombic to tetragonal transition occurs at  $y \sim 0.4$ .



**Figure 1.** Scanning electron micrographs showing (a) a ceramic pellet of  $\text{YBa}_2\text{Cu}_3\text{O}_{6.94}$  before corrosion, (b) the same sample after its exposure to water for 2 days at room temperature, and (c) a  $\text{Y}_{0.6}\text{Ca}_{0.4}\text{Ba}_{1.6}\text{La}_{0.4}\text{Cu}_3\text{O}_{6.96}$  pellet sample after soaking for 30 days in water at room temperature.

Samples of  $\text{Y}_{1-y}\text{Ca}_y\text{Ba}_{2-y}\text{La}_y\text{Cu}_3\text{O}_{7-\delta}$  were synthesized by solid state reaction methods.<sup>10,14</sup> To explore the environmental reactivity characteristics of the substituted compounds, pellet and powder samples were exposed to liquid water at 25 °C and water vapor at 75 °C for various lengths of time. Scanning electron microscopy (SEM) images were recorded for the samples before and after the water treatment. The results of the SEM study are shown in Figure 1. Here, the unsubstituted pellet sample becomes completely coated with  $\text{BaCO}_3$  crystallites after soaking in water for 2 days, indicating that the sample has decomposed to a significant extent. The formation of the carbonate salt can be traced to the presence of the atmospheric  $\text{CO}_2$  in the chamber as documented previously.<sup>12</sup> On the other hand, pellet samples of  $\text{Y}_{0.7}\text{Ca}_{0.3}\text{Ba}_{1.7}\text{La}_{0.3}\text{Cu}_3\text{O}_{6.95}$  and  $\text{Y}_{0.6}\text{Ca}_{0.4}\text{Ba}_{1.6}\text{La}_{0.4}\text{Cu}_3\text{O}_{6.96}$  appear to be remarkably stable, as almost no reaction with water was observed after 1 month of soaking. In addition to the electron microscopy results, SQUID, 4-probe conductivity, and X-ray powder diffraction (XRD) measurements were obtained before and after the water treatment. Accordingly, all methods demonstrated in a convincing fashion that bulk samples of  $\text{Y}_{1-y}\text{Ca}_y\text{Ba}_{2-y}\text{La}_y\text{Cu}_3\text{O}_{7-\delta}$  display marked increases in their corrosion resistance as compared to the parent compound. Within the  $\text{Y}_{1-y}\text{Ca}_y\text{Ba}_{2-y}\text{La}_y\text{Cu}_3\text{O}_{7-\delta}$  series, the corrosion resistance can be enhanced by increasing  $y$ . Greater than a 100-fold increase

- <sup>†</sup> Department of Chemistry and Biochemistry.  
<sup>‡</sup> Center for Materials Science and Engineering.  
(1) Zhou, J. P.; McDevitt, J. T. *Chem. Mater.* **1992**, *4*, 953.  
(2) Zhou, J. P.; Riley, D. R.; Manthiram, A.; Arendt, M.; Schmerling, M.; McDevitt, J. T. *Appl. Phys. Lett.* **1993**, *4*, 548.  
(3) Barkatt, A.; Hojaji, H.; Amarakoon, V. R. W.; Fagan, J. G. *MRS Bull.* **1993**, *9*, 45.  
(4) Rosamilia, J. M.; Miller, B.; Schnemeyer, L. F.; Waszczak, J. V.; O'Bryan, H. M., Jr. *J. Electrochem. Soc.* **1987**, *134*, 1863.  
(5) (a) Black, R. D.; Early, T. A.; Roemer, P. B.; Mueller, O. M.; Mogro-Campero, A.; Turner, L. G.; Johnson, G. A. *Science* **1993**, *259*, 793. (b) Bedekar, M. M.; Safari, A.; Wilber, W. *Physica C* **1992**, *202*, 42. (c) Narita, H.; Hanano, T.; Nakamura, K. *J. Appl. Phys.* **1992**, *72*, 5778.  
(6) Capponi, J. J.; Chailout, C.; Hewat, A. W.; Lijay, P.; Marrezio, M.; Nguyen, N.; Ravear, B.; Sopubeyroux, J. L.; Tholence, J. L.; Tournier, R. *Europhys. Lett.* **1987**, *3*, 1301.  
(7) Jorgensen, J. D.; Veal, B. W.; Paulikas, A. P.; Nowicki, L. J.; Crabtree, G. W.; Claus, H.; Kwok, W. K. *Phys. Rev. B* **1990**, *41*, 1863.  
(8) Brown, I. D. *J. Solid State Chem.* **1991**, *90*, 1952.  
(9) Goodenough, J. B.; Manthiram, A. *J. Solid State Chem.* **1991**, *92*, 231.  
(10) Zhou, J. P.; Riley, D. R.; McDevitt, J. T. *Chem. Mater.* **1993**, *5*, 361.  
(11) Zhou, J. P.; McDevitt, J. T. *Solid State Commun.* **1993**, *86*, 11.  
(12) Yan, M. F.; Barns, R. L.; O'Bryan, H. M., Jr.; Gallagher, P. K.; Sherwood, R. C.; Jin, S. *Appl. Phys. Lett.* **1987**, *51*, 532.  
(13) Manthiram, A.; Tang, X. X.; Goodenough, J. B. *Phys. Rev. B* **1988**, *37*, 3734.  
(14) Manthiram, A.; Goodenough, J. B. *Physica C* **1989**, *159*, 760.

**Table 1.** Summary of Data for the High- $T_c$  Compounds

sample <sup>a</sup>	$T_c$ (K)	structure (O/T) <sup>b</sup>	lifetime (days) <sup>c</sup>
YBa <sub>2</sub> Cu <sub>3</sub> O <sub>6.94</sub>	90	O	2.0
YBa <sub>2</sub> Cu <sub>3</sub> O <sub>6.59</sub>	60	O	4.0
YBa <sub>2</sub> Cu <sub>3</sub> O <sub>6.05</sub>		T	0.5
Y <sub>0.9</sub> Ca <sub>0.1</sub> Ba <sub>1.9</sub> La <sub>0.1</sub> Cu <sub>3</sub> O <sub>6.97</sub>	85	O	5.0
Y <sub>0.8</sub> Ca <sub>0.2</sub> Ba <sub>1.8</sub> La <sub>0.2</sub> Cu <sub>3</sub> O <sub>6.96</sub>	83	O	10.0
Y <sub>0.7</sub> Ca <sub>0.3</sub> Ba <sub>1.7</sub> La <sub>0.3</sub> Cu <sub>3</sub> O <sub>6.95</sub>	80	O <sup>d</sup>	>80.0
Y <sub>0.6</sub> Ca <sub>0.4</sub> Ba <sub>1.6</sub> La <sub>0.4</sub> Cu <sub>3</sub> O <sub>6.96</sub>	80	T	>150.0

<sup>a</sup> Oxygen contents from iodometric titrations<sup>17</sup> and  $T_c$  values from 4-probe and SQUID measurements. <sup>b</sup> Orthorhombic vs tetragonal crystal symmetry. <sup>c</sup> Lifetimes were estimated by XRD as the sample exposure time necessary to degrade 50% of sample. <sup>d</sup> This specimen is close to the orthorhombic-to-tetragonal transition.

in the lifetime of Y<sub>0.6</sub>Ca<sub>0.4</sub>Ba<sub>1.6</sub>La<sub>0.4</sub>Cu<sub>3</sub>O<sub>6.96</sub> as compared to YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6.94</sub> is noted as illustrated in Table 1.

In addition to the bulk reactivity studies mentioned above, we have also evaluated the environmental reactivity characteristics of high- $T_c$  films. In this regard, the method of laser ablation was utilized to deposit *c*-axis oriented films of YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7- $\delta$</sub>  and Y<sub>0.6</sub>Ca<sub>0.4</sub>Ba<sub>1.6</sub>La<sub>0.4</sub>Cu<sub>3</sub>O<sub>7- $\delta$</sub>  onto MgO(100) substrates as 2000 Å thick films. The typical specimens of this type display transition temperatures of 90 and 80 K, respectively.

Aside from a few qualitative descriptions of the reactivity of high- $T_c$  films,<sup>15</sup> little quantitative information is currently available in the literature related to the environmental degradation behavior of thin film samples. To evaluate the reactivity of the superconductor thin-film specimens, resistivity vs time data were recorded for the two materials as they were simultaneously exposed to water vapor that was equilibrated at 75 °C. In this regard, films of YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7- $\delta$</sub>  degraded rapidly over a period of 2 h. From the physical appearance of the film, it was observed that the passage of current through the superconductor served to strongly accelerate the corrosion processes, as seen by selective degradation in the vicinity around the electrodes. After stopping the passage of current through the YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7- $\delta$</sub>  film, more gradual degradation of the film was noted in regions remote from the contacts. On the other hand, the Y<sub>0.6</sub>Ca<sub>0.4</sub>Ba<sub>1.6</sub>La<sub>0.4</sub>Cu<sub>3</sub>O<sub>7- $\delta$</sub>  film sample showed very little change in its resistance over a period of 10 days.

(15) Chang, C.-A. *Appl. Phys. Lett.* **1988**, *53*, 1113.

Within the Y<sub>1- $y$</sub> Ca <sub>$y$</sub> Ba<sub>2- $y$</sub> La <sub>$y$</sub> Cu<sub>3</sub>O<sub>7- $\delta$</sub>  class of compounds, measurements of the lattice parameter indicate that the degree of orthorhombicity is decreased with increasing amount of substitution.<sup>14</sup> Interestingly, the most stable compound in the series is the tetragonal material, Y<sub>0.6</sub>Ca<sub>0.4</sub>Ba<sub>1.6</sub>La<sub>0.4</sub>Cu<sub>3</sub>O<sub>6.96</sub> ( $a = b = 3.869$  Å,  $c = 11.622$  Å), in which the oxygen atoms are disordered in the Cu(1)O<sub>x</sub> planes. The dramatic increase in chemical stability may arise from blocking solution access of protic species into the interior of the superconductor by the presence of oxygen at both the *a*- and *b*-axes of the Cu(1)O<sub>x</sub> planes. Alternatively, the release of internal stress and strain factors may play an important role, and/or the formation of an oxygen rich surface ( $\sim 15$ – $30$  Å) detected by X-ray photoemission depth profile studies may serve to stabilize the material. Surface passivation for the protection of stainless steel has been shown to enhance the environmental stability of this material.<sup>16</sup> Careful studies are now in progress to determine which of the factors is responsible for the observed behavior.

From the data presented in this paper, it is clear that the cation substitution method represents a successful new strategy for the preparation of chemically stable, high- $T_c$  bulk and thin-film samples. The availability of these stable cuprate phases may facilitate the more rapid commercialization of high- $T_c$  thin-film structures and devices.

**Acknowledgment.** This research was supported by the National Science Foundation, the Office of Naval Research, and the Welch Foundation. Professors John B. Goodenough, Allen J. Bard, John T. Markert, and Hugo Steinfink are thanked for the use of their instruments.

**Supplementary Material Available:** Resistivity vs temperature curve, X-ray diffraction data, resistivity vs water vapor exposure time curves, and optical photographs of degraded films (6 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

(16) Bayliss, D. A.; Chander, K. A. *Textbook of Steelwork Corrosion Control*; Elsevier Applied Science: New York, 1991; p 11.

(17) Manthiram, A.; Swinnea, J. S.; Sui, Z. T.; Steinfink, H.; Goodenough, J. B. *J. Am. Chem. Soc.* **1987**, *109*, 6667.

Applied Physics Letter

(3/2/95)

Improved Corrosion Resistance of Cation Substituted  
 $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$

Ji-Ping Zhou, Steven M. Savoy, Rung-Kuang Lo, Jianai Zhao,  
Mark Arendt, Y.T. Zhu,<sup>a)</sup> A. Manthiram<sup>a)</sup> and John T. McDevitt,\*

Department of Chemistry and Biochemistry, The University of Texas at Austin,  
Austin, Texas 78712-1167

Abstract

A cosubstitution of  $\text{Ca}^{2+}$  for  $\text{Y}^{3+}$  and  $\text{La}^{3+}$  for  $\text{Ba}^{2+}$  in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  is found to improve the corrosion resistance of this high- $T_c$  superconductor. The reactivity characteristics of bulk and thin film samples of  $\text{Y}_{1-z}\text{Ca}_z\text{Ba}_{2-y}\text{La}_y\text{Cu}_3\text{O}_{7-\delta}$  indicate that the corrosion resistance in water environments increases with increasing degree of cation substitution up to  $z = y = 0.4$ . The composition of  $\text{Y}_{0.6}\text{Ca}_{0.4}\text{Ba}_{1.6}\text{La}_{0.4}\text{Cu}_3\text{O}_{6.96}$  with a  $T_c$  of 80 K is found to be at least 100 times more stable than  $\text{YBa}_2\text{Cu}_3\text{O}_{6.94}$ . Possible contributing factors that could be responsible for the marked improvement in the corrosion resistance of this high- $T_c$  phase are discussed.

---

<sup>a)</sup>Center of Materials Science and Engineering, University of Texas at Austin,  
Austin, TX 78712-1063.

One of the major problems that has slowed technological developments of copper oxide superconductors has been their tendency to degrade chemically when exposed to water, acids,  $\text{CO}_2$  and  $\text{CO}$ .<sup>1-3</sup> Of the technologically important superconductors with transition temperatures above 77 K (i.e.  $\text{YBa}_2\text{Cu}_3\text{O}_7$ ,  $\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ ,  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$  and  $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_9$ ),  $\text{YBa}_2\text{Cu}_3\text{O}_7$  is the preferred material for thin film applications.<sup>4</sup> Unfortunately,  $\text{YBa}_2\text{Cu}_3\text{O}_7$  displays the least corrosion resistance among the cuprates.<sup>1</sup>

The  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  phase has an oxygen-deficient perovskite structure with a layer sequence of  $\text{Cu}(1)\text{O}_x\text{-BaO-Cu}(2)\text{O}_2\text{-Y-Cu}(2)\text{O}_2\text{-BaO-Cu}(1)\text{O}_x$  along the c-axis.<sup>5</sup> In the  $\text{Cu}(1)\text{O}_x$  layer, oxygen atoms are ordered along the b-axis with vacancies existing along the a-axis that form open channels which run parallel to the b-axis. Protic species can penetrate into the lattice via these channels and react with oxygen leading to structural instability.<sup>6</sup> This type of reactivity has been identified by proton NMR studies of high- $T_c$  specimens in the early stages of corrosion.<sup>7</sup> Moreover, it has been shown previously that changes in oxygen content in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  ( $0 < \delta < 1$ ) serve to influence the degree of bond length mismatch.<sup>8</sup> We have shown recently that  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  samples having intermediate oxygen contents corrode more slowly than do samples with either higher or lower oxygen contents.<sup>9,10</sup> This behavior cannot be explained satisfactorily along the lines of copper valence as previously hypothesized.<sup>11</sup> Rather, lattice defects and internal stress and strain phenomena appear to be important factors dictating the decomposition kinetics for this material.

Consequently, cation substitutions in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  which relieve the internal stresses arising from bond length mismatch may provide an effective strategy to improve the corrosion resistance of this technologically important

superconductor. To date, a large number of studies have been completed on cation and anion substitution reactions into the  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  structure. Many of the previous reports have focused on the structure-property relationships.<sup>12-15</sup> In most cases of the anion substitutions, a dramatic decrease in  $T_C$  was noted and/or the formation of impurities was found.<sup>12</sup> On the other hand, a family of isostructural materials with rare earth ions substituted into the Y site exhibited only minor changes in  $T_C$  for most cases.<sup>13</sup> Since there are no oxygen atoms in the yttrium layer, the substitutions at this site are expected to result in only modest changes in the internal stresses. Substitutions that lead to improved bond length matching between the Ba-O and the  $\text{Cu}(2)\text{O}_2$  layers and relieve the internal stresses should be more important.<sup>14-17</sup> Since previous studies have shown that substitutions into the Cu site normally decrease  $T_C$  in a dramatic fashion,<sup>14</sup> our initial efforts were focused toward chemical substitutions at the Ba site. Incorporation of  $\text{La}^{3+}$  into  $\text{YBa}_{2-y}\text{La}_y\text{Cu}_3\text{O}_{7-\delta}$  has been shown<sup>16</sup> to cause a rapid decrease in  $T_C$  due to a disordering of oxygen in the  $\text{Cu}(1)\text{O}_x$  plane and an accompanying transfer of holes from the active  $\text{Cu}(2)\text{O}_2$  sheets to the inactive  $\text{Cu}(1)\text{O}_x$  planes. However, a cosubstitution of  $\text{Ca}^{2+}$  for  $\text{Y}^{3+}$  and  $\text{La}^{3+}$  for  $\text{Ba}^{2+}$  in the  $\text{Y}_{1-y}\text{Ca}_y\text{Ba}_{2-y}\text{La}_y\text{Cu}_3\text{O}_{7-\delta}$  system has been found<sup>17</sup> to maintain the  $T_C$  above 80 K, in spite of an orthorhombic to tetragonal transition which occurs at  $y \sim 0.4$ .

Samples of  $\text{Y}_{1-y}\text{Ca}_y\text{Ba}_{2-y}\text{La}_y\text{Cu}_3\text{O}_{7-\delta}$  were synthesized as reported elsewhere.<sup>17</sup> Environmental reactivity characteristics were evaluated by exposing the pellet and powder samples to water solution at  $25^\circ\text{C}$  and to water vapor at  $75^\circ\text{C}$  for various lengths of time.<sup>1,9,10</sup> Electron microscopic studies reveal that the surface of a pellet of the unsubstituted  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  was severely degraded as the sample becomes completely coated with  $\text{BaCO}_3$  crystallites after exposing it for 2 days to aerated water solution. On the other

hand, pellets of the cosubstituted  $\text{Y}_{0.7}\text{Ca}_{0.3}\text{Ba}_{1.7}\text{La}_{0.3}\text{Cu}_3\text{O}_{6.95}$  and  $\text{Y}_{0.6}\text{Ca}_{0.4}\text{Ba}_{1.6}\text{La}_{0.4}\text{Cu}_3\text{O}_{6.96}$  appear to be remarkably stable since almost no reaction with water solution occurred even after one month of exposure. In addition to the electron microscopy results, magnetic susceptibility, 4-probe conductivity and X-ray powder diffraction (XRD) measurements were obtained before and after the water treatment. All results demonstrate in a convincing fashion that bulk samples of  $\text{Y}_{1-y}\text{Ca}_y\text{Ba}_{2-y}\text{La}_y\text{Cu}_3\text{O}_{7-\delta}$  display marked increases in their corrosion resistance compared to the parent compound,  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ .

To quantify the reactivity characteristics of these materials, their corrosion lifetimes were estimated by examining the samples by XRD after exposing them to water for different lengths of time. The results are given in Table 1. The sample lifetime increases with increasing  $y$  in  $\text{Y}_{1-y}\text{Ca}_y\text{Ba}_{2-y}\text{La}_y\text{Cu}_3\text{O}_{7-\delta}$ . More than a 100-fold increase in the lifetime is found on going from  $\text{YBa}_2\text{Cu}_3\text{O}_{6.94}$  to  $\text{Y}_{0.6}\text{Ca}_{0.4}\text{Ba}_{1.6}\text{La}_{0.4}\text{Cu}_3\text{O}_{6.96}$ .

Aside from a few qualitative descriptions of the reactivity of high- $T_c$  films,<sup>19</sup> little quantitative information is currently available in the literature related to the environmental degradation behavior of thin film specimens. Consequently, we have evaluated the reactivity behavior of cation substituted thin film samples. The method of laser ablation was utilized to deposit 2000 Å thick films of c-axis oriented  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  and  $\text{Y}_{0.6}\text{Ca}_{0.4}\text{Ba}_{1.6}\text{La}_{0.4}\text{Cu}_3\text{O}_{7-\delta}$  onto MgO (100) substrates. The films displayed  $T_c$  values near 90 K and 80 K, respectively. The variation of resistivity with time was recorded for both the films as they were simultaneously exposed to water vapor equilibrated at 75°C. The  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  film degraded rapidly over a period of two hours as illustrated in Figure 1a. On the other hand, the  $\text{Y}_{0.6}\text{Ca}_{0.4}\text{Ba}_{1.6}\text{La}_{0.4}\text{Cu}_3\text{O}_{7-\delta}$  film showed very little change in its resistance properties over a period of 8 days as

illustrated in Figure 1b. From the physical appearance of the film, it is clear that the passage of current through the superconductor accelerates the corrosion processes during 4-probe resistivity measurements. This behavior is evident from the selective degradation which occurs in the vicinity around the electrodes. After terminating the passage of current through the  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  film, more gradual degradation of the film was noted in regions remote from the contacts as shown in Figure 2.

To further explore the reactivity characteristics of the films, XPS depth profile studies were completed using film specimens that were exposed to 5%  $\text{H}_2\text{O}/\text{CH}_3\text{CN}$  solution for 5 minutes. Whereas the  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  film showed a carbon containing degradation layer on the surface, the top most region of the  $\text{Y}_{0.6}\text{Ca}_{0.4}\text{Ba}_{1.6}\text{La}_{0.4}\text{Cu}_3\text{O}_{7-\delta}$  film was found to be free of this feature. Moreover, sample of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  kept in the air for a few months displayed an accumulation of carbon contamination layer on the surface ( $\sim 30\text{-}50\text{\AA}$ ). However, only a very thin carbon degradation layer ( $< 3\text{\AA}$ ) is noted for the  $\text{Y}_{0.6}\text{Ca}_{0.4}\text{Ba}_{1.6}\text{La}_{0.4}\text{Cu}_3\text{O}_{7-\delta}$  films treated in a similar fashion. The presence of these surface carbon layers is consistent with the formation of surface layers of  $\text{BaCO}_3$  (vide supra).

Within the  $\text{Y}_{1-y}\text{Ca}_y\text{Ba}_{2-y}\text{La}_y\text{Cu}_3\text{O}_{7-\delta}$  class of compounds, the lattice parameter measurements indicate that the degree of orthorhombicity decreases with increasing  $y$ . Interestingly, we find the most stable compound in the series to be the tetragonal phase,  $\text{Y}_{0.6}\text{Ca}_{0.4}\text{Ba}_{1.6}\text{La}_{0.4}\text{Cu}_3\text{O}_{6.96}$  ( $a = b = 3.869\text{ \AA}$ ,  $c = 11.622\text{ \AA}$ ), in which the oxygen atoms are disordered in the  $\text{Cu}(1)\text{O}_x$  planes. Thus, the dramatic increase in chemical stability may arise due to a blocking of the access of protic species into the interior of the superconductor by the disordering of oxygen atoms in  $\text{Cu}(1)\text{O}_x$  planes. Alternatively, the relief of internal stresses and/or the formation of an oxygen rich surface caused by the

chemical substitutions may be responsible for the remarkable increase in the corrosion resistance.

It is clear from data presented here that simple cation substitutions can be used to achieve improved corrosion resistance of high- $T_C$  phases. Having identified an effective strategy for improving the environmental stability of cuprate compounds, it should be possible now to optimize both superconductivity and stability properties for a given application. Work is now in progress to achieve such an objective. The discovery of new corrosion resistant cuprate superconductors may facilitate a more rapid commercialization of high- $T_C$  thin film structures and devices.

**Acknowledgment.** This research was supported by the National Science Foundation, and the Office of Naval Research. Professors John B. Goodenough, Allen J. Bard, John M. White and Hugo Steinfink are thanked for use of their instruments.

## References

- (1) J.P. Zhou, D.R. Riley, A Manthiram, M. Arendt, M. Schmerling, J.T. McDevitt, Appl. Phys. Lett. **4**, 548 (1993).
- (2) A. Barkatt, H. Hojaji, V.R.W. Amarakoon, J.G. Fagan, MRS Bulletin, **9**, 45 (1993).
- (3) J.M. Rosamilia, B. Miller, L.F. Schnemeyer, J.V. Waszczak, H.M. O'Bryan Jr. J. Electrochem. Soc. **134**, 1863 (1987).
- (4) (a) R.D. Black, T.A. Early, P.B. Roemer, O.M. Mueller, A. Morgo-Campero, L.G. Turner, G.A. Johnson, Science **259**, 793 (1993). (b) M.M. Bedekar, A. Safari, W. Wilber, Physica C, **202**, 42 (1992). (c) H. Narita, T. Hanano, K. Nakamura, J. Appl. Phys. **72**, 5778 (1992).
- (5) J.D. Jorgensen, B.W. Veal, A.P. Paulikas, L.J. Nowicki, G.W. Crabtree, H. Claus, W.K. Kwok, Phys. Rev. B **41**, 1863 (1990).
- (6) J.G. Thompson, B.G. Hyde, R.L. Withers, J.S. Anderson, J.D. Fitz Gerald, J. Bitmead, M.S. Paterson, A.M. Stewart, Mat. Res. Bull. **22**, 1715 (1987).
- (7) H. Nishihara, N. Nishida, T. Takabatake, K. Kishio, A. Ohtomo, K. Hayashi, M. Ishikawa, Y. Nakazawa, K-I. Koga, T. Tamegai, K. Kitazawa, Jap. J. Appl. Phys. **27**, 1652 (1988).
- (8) I.D. Brown, J. Solid State Chem. **90**, 1952 (1991).
- (9) J.P. Zhou; D.R. Riley, J.T. McDevitt, Chem. Mater. **5**, 361 (1993).
- (10) J.P. Zhou, J.T. McDevitt, Solid State Commu. **86**, 11 (1993).
- (11) M.F. Yan, R.L. Barns, H.M. O'Bryan Jr, P.K. Gallagher, R.C. Sherwood, S. Jin, Appl. Phys. Lett. **51**, 532 (1987).
- (12) Y.M. Yarmoshenko, V.A. Trofimova, L.V. Elokhina, E.Z. Kurmaev, S. Butorin, R. Cloots, M. Ausloss, Physica C **211**, 29 (1993).

- (13) P.H. Hor, R.L. Ming, Y.Q. Wang, L. Gao, Z.J. Huang, J. Bechtold, K. Forster, C.W. Chu, Phys. Rev. Lett. **58**, 1891 (1987).
- (14) Q. Huang, R.J. Cava, A. Santoro, J.J. Krajewski, W.F. Peck, Physica C **193**, 196 (1992).
- (15) S.A. Sunshine, L.F. Schneemeyer, T. Siegrist, D.C. Douglass, J.V. Waszczak, R.J. Cava, E.M. Gyorgy, D.W. Murphy, Chem. Mater. **1**, 331 (1989).
- (16) A. Manthiram, X.X. Tang, J.B. Goodenough, Phys. Rev. B , **37**, 3734 (1988).
- (17) A. Manthiram, J.B. Goodenough, Physica C **159**, 760 (1989).
- (18) A. Manthiram, J.S. Swinnea, Z.T. Sui, H. Steinfink, J.B. Goodenough, J. Am. Chem. Soc. **109**, 6667 (1987).
- (19) C.-A. Chang, Appl. Phys. Lett. **53**, 1113 (1988).

**Table 1** Summary of Data for the High- $T_C$  Compounds

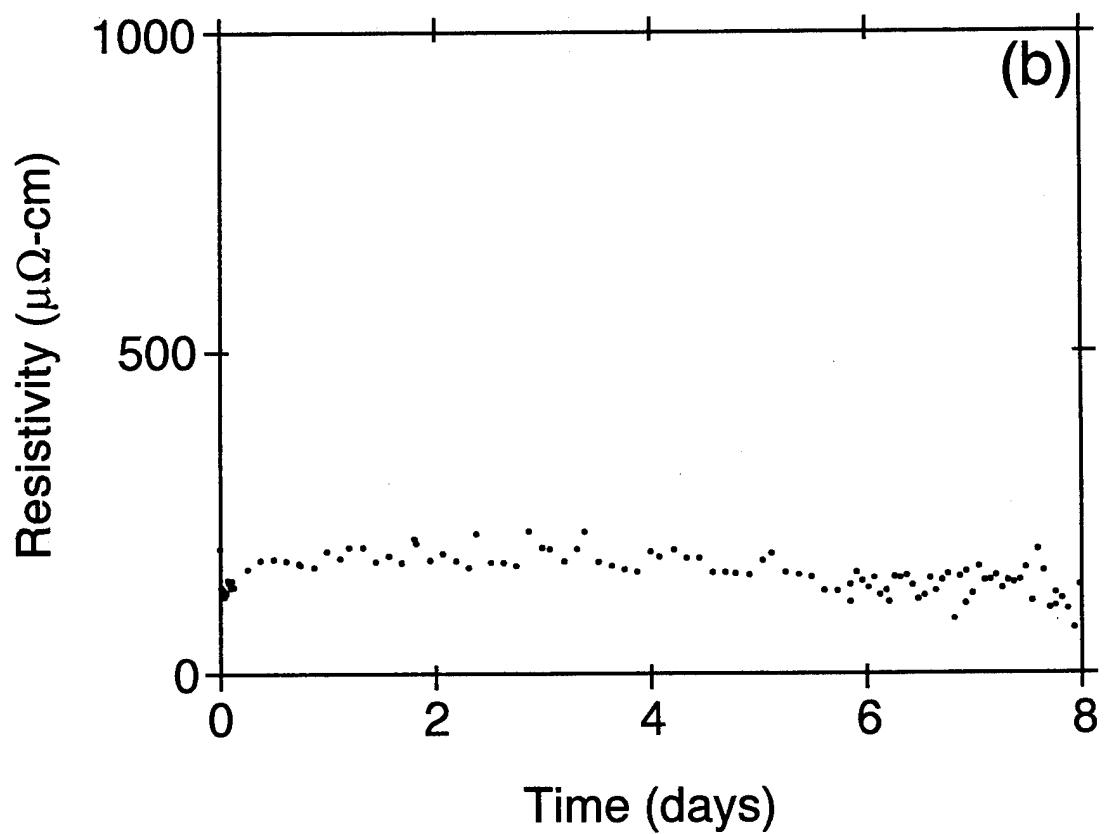
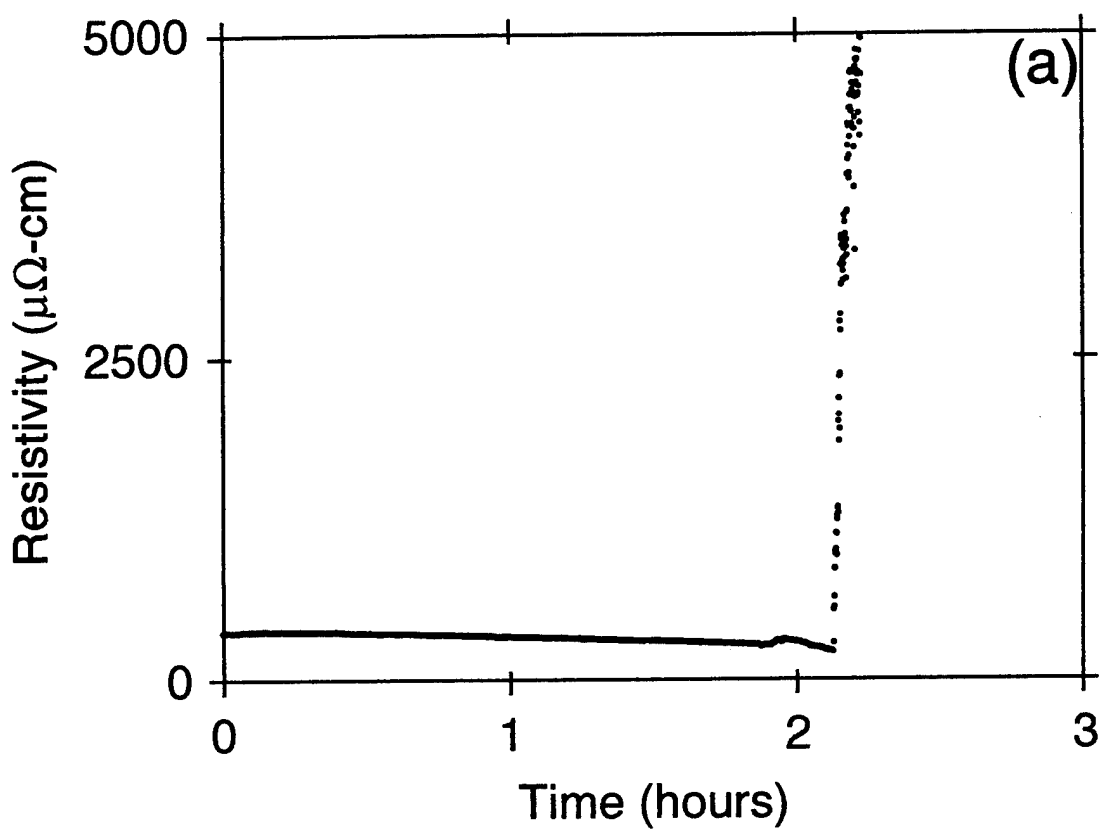
Sample <sup>a</sup>	$T_C$ (K)	Structure (O/T) <sup>b</sup>	Lifetime (days) <sup>c</sup>
YBa <sub>2</sub> Cu <sub>3</sub> O <sub>7</sub>	90	O	2.0
YBa <sub>2</sub> Cu <sub>3</sub> O <sub>6.59</sub>	60	O	4.0
YBa <sub>2</sub> Cu <sub>3</sub> O <sub>6.05</sub>	--	T	0.5
Y <sub>0.9</sub> Ca <sub>0.1</sub> Ba <sub>1.9</sub> La <sub>0.1</sub> Cu <sub>3</sub> O <sub>6.97</sub>	85	O	5.0
Y <sub>0.8</sub> Ca <sub>0.2</sub> Ba <sub>1.8</sub> La <sub>0.2</sub> Cu <sub>3</sub> O <sub>6.96</sub>	83	O	10.0
Y <sub>0.7</sub> Ca <sub>0.3</sub> Ba <sub>1.7</sub> La <sub>0.3</sub> Cu <sub>3</sub> O <sub>6.95</sub>	80	O <sup>d</sup>	>80.0
Y <sub>0.6</sub> Ca <sub>0.4</sub> Ba <sub>1.6</sub> La <sub>0.4</sub> Cu <sub>3</sub> O <sub>6.96</sub>	80	T	>150.0

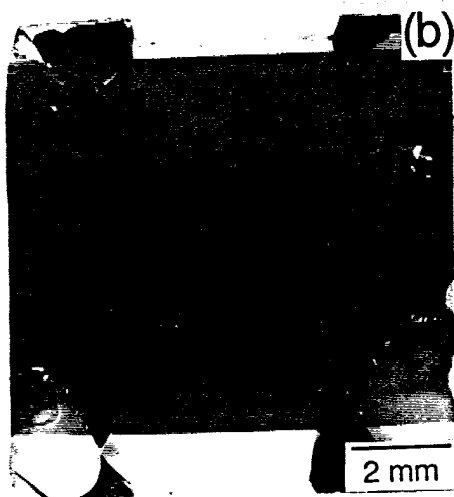
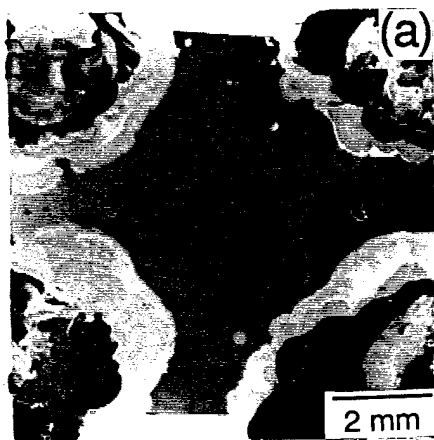
- a** Oxygen contents from iodometric titrations and  $T_C$  values from 4-point probe and SQUID measurements.
- b** Orthorhombic vs. tetragonal crystal symmetry.
- c** Lifetimes were estimated by XRD as the sample exposure time necessary to degrade 50% of sample.
- d** This specimen possessed a transitional structure with lattice symmetry intermediate between orthorhombic vs. tetragonal.

## Figure Captions

**Figure 1.** Resistivity vs. time measurements for (a) a  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  film in  $75^\circ\text{C}$  water vapor showing the degradation which occurs over a period of 2 hours and (b) a  $\text{Y}_{0.6}\text{Ca}_{0.4}\text{Ba}_{1.6}\text{La}_{0.4}\text{Cu}_3\text{O}_{7-\delta}$  film in same environment which shows little sign of degradation over a period of 8 days. Both films were  $2000 \text{ \AA}$  thick and were supported on  $\text{MgO}$  (100) substrates. Alternating polarity quasi d.c. bias currents of  $5.0 \times 10^{-5}$  amps were utilized for the measurements.

**Figure 2.** Optical photographs showing (a) a  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  film and (b) a  $\text{Y}_{0.6}\text{Ca}_{0.4}\text{Ba}_{1.6}\text{La}_{0.4}\text{Cu}_3\text{O}_{7-\delta}$  film after their simultaneous exposure to  $75^\circ\text{C}$  water vapor for 10 days.





[Inorganic Gordon Conference 7/94]  
[Invited Lecture & Poster Session]

## CHEMICALLY TAILORED CORROSION RESISTANT HIGH- $T_C$ PHASES

John T. McDevitt, Ji-Ping Zhou, Steven M. Savoy, Jianai Zhao  
and David R. Riley

Department of Chemistry and Biochemistry, The University of Texas at  
Austin, Austin, Texas 78712-1167

### Abstract

In order to produce chemically and environmentally stable forms of  $YBa_2Cu_3O_{7-\delta}$  superconductors, a series of cation substitution reactions were completed. It was found that the corrosion resistance increases with increasing  $y$  in  $Y_{1-y}Ca_yBa_{2-y}La_yCu_3O_{7-\delta}$ . The chemical degradation behavior in water for both bulk and thin film samples of  $Y_{1-y}Ca_yBa_{2-y}La_yCu_3O_{7-\delta}$  has been obtained along with similar data for the unsubstituted compound,  $YBa_2Cu_3O_{7-\delta}$ . The composition of  $Y_{0.6}Ca_{0.4}Ba_{1.6}La_{0.4}Cu_3O_{6.96}$  with a  $T_C = 80$  K was found to be at least 100 times more stable than  $YBa_2Cu_3O_{6.94}$ . The availability of these stable cuprate phases may facilitate the more rapid commercialization of high- $T_C$  thin film structures and devices.

[IBM Yorktown Heights]  
[Invited Lecture, 4/95]

**MOLECULAR AND CRYSTAL ENGINEERING OF HIGH-TC  
STRUCTURES AND DEVICES**

**John T. McDevitt**

**Department of Chemistry and Biochemistry, The University of Texas  
at Austin, Austin, Texas 78712-1167**

**Abstract**

In an attempt to foster more rapid developments in the areas of high- $T_c$  superconductivity and macromolecular electronic devices, our group has recently initiated a series of studies designed to explore fundamental issues related to the chemistry of high- $T_c$  compounds. Knowledge in this regard is particularly important because the poor reactivity problems and materials processing limitations have hampered developments in this area. From our studies, we have identified lattice stress and strain as important variables which influence the environmental reactivity of the most popular high- $T_c$  superconductor compound,  $YBa_2Cu_3O_7$ . Using solid-state substitution reactions, we have tailored the high- $T_c$  lattice so as to relieve the internal stress and strain. Consequently, formulations such as  $Y_{0.6}Ca_{0.4}Ba_{1.6}La_{0.4}Cu_3O_7$  have been prepared that exhibit both excellent stability and good superconducting properties. Moreover, we have developed methods that can be used for the spontaneous adsorption of amine molecules onto the surfaces of cuprate structures. Armed with detailed fundamental knowledge of the surface and interface properties of the high- $T_c$  materials, our group has completed the initial studies in a new area of research which involves the study of superconductor elements that are derivatized with molecular compounds. Consequently, we have designed, fabricated and tested the first two classes of molecule/superconductor devices. Through the combination of carefully chosen photoactive and electroactive molecular assemblies with high- $T_c$  electronic devices, we have shown that it is possible to engineer the molecular layer so that a number of structures can be prepared to serve a variety of applications.

[J. of Supercon. 1995, 8, in press]

PHYSICAL AND CHEMICAL PROPERTIES OF  $(Y_{1-x}Ca_x)(Ba_{2-x}La_x)Cu_3O_{7-\delta}$

J.P. Zhou<sup>a</sup>, J.-S. Zhou<sup>b</sup>, J.B. Goodenough<sup>b</sup> and J.T. McDevitt<sup>a</sup>

<sup>a</sup>Department of Chemistry and Biochemistry, <sup>b</sup>Center for Materials Science and Engineering, University of Texas at Austin, TX 78712

Abstract

The metallic conductivity of both the  $CuO_2$  sheets and the  $CuO_x$  chains of  $YBa_2Cu_3O_{7-\delta}$  has been established. We have used double doping in  $(Y_{1-x}Ca_x)(Ba_{2-x}La_x)Cu_3O_{7-\delta}$  to destroy the  $CuO_{1-\delta}$  chains while keeping constant the total oxidation of the Cu-O array. A  $T_C \approx 90$  K decreases with increasing  $x$  to  $T_C \approx 80$  K at  $x \approx 0.35$  and remains at 80 K on crossing the orthorhombic-tetragonal phase boundary associated with a break-up of the chain segments. A break-up of the chain segments allows us to establish the temperature dependence of the Seebeck coefficient  $a(t)$  due to the  $CuO_2$  sheets and by difference of the  $CuO_{1-\delta}$  chains in  $YBa_2Cu_3O_{7-\delta}$ . The shape of the positive  $a(t)$  curve for the  $CuO_2$  sheets is similar to that found for  $La_{1.85}Sr_{0.15}CuO_4$ ; the chain contribution to  $a(t)$  in  $YBa_2Cu_3O_{7-\delta}$  is negative, but shows a similar low-temperature enhancement of its magnitude. At low temperature, the  $CuO_{1-\delta}$  chains stabilize a charge-density wave and the  $CuO_2$  sheets become superconducting. We also show that double doping enhances significantly the chemical stability of the superconductive phase. The origin of the chemical stability and of the behavior of  $a(t)$  is interpreted.

[Accepted April 3, 1995]

[J. Am. Chem. Soc.]

**SURVEYING THE SURFACE COORDINATION CHEMISTRY OF A  
SUPERCONDUCTOR: SPONTANEOUS ADSORPTION OF  
MONOLAYER FILMS OF REDOX-ACTIVE "LIGANDS" ON  
YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub>**

**Kaimin Chen and Chad A. Mirkin\***

**Department of Chemistry, Northwestern University, 2145 Sheridan  
Rd., Evanston, IL 60208**

**Rung-Kuang Lo, Jianai Zhao, and John T. McDevitt\***

**Department of Chemistry and Biochemistry, University of Texas at  
Austin, Austin, TX 78712.**

**Abstract**

A preliminary survey of the surface coordination chemistry of YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> has been completed using a series of redox-active ligands containing alkyl amine, aryl amine, thiol, phosphine, amide, and alcohol functionalities. Cyclic voltammetry, atomic force microscopy, and resistivity measurements were utilized to evaluate the influence of these adsorbate molecules on the properties of the high-T<sub>C</sub> superconductor. Evidence supporting the strong adsorption of molecules with alkyl amine, aryl amine and thiol functionalities is reported. Resistivity vs. temperature measurements for the YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> and modified YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> shows that chemical modification does not significantly lower T<sub>C</sub> for the superconductor. The work reported herein is the first example of the direct chemical modification of the surface of a superconductor with a monolayer of a molecular reagent. Moreover, the spontaneous adsorption of redox-active alkyl amines, aryl amines, and thiols has been shown to produce stable and robust monolayer films with no apparent damage to the underlying cuprate material.

\*Authors to whom correspondence should be addressed.

[J. Am. Chem. Soc. 1994, 116, 9389-9390]

**CHEMICALLY TAILORED CORROSION RESISTANT HIGH- $T_c$   
PHASES**

Ji-Ping Zhou<sup>a</sup>, Steven M. Savoy<sup>a</sup>, Jianai Zhao<sup>a</sup>, David R. Riley<sup>a</sup>,  
Y.T. Zhu<sup>b</sup>, A. Manthiram<sup>b</sup>, Damon Borich<sup>a</sup> and John T. McDevitt<sup>a\*</sup>

Department of Chemistry and Biochemistry<sup>a</sup>, Center for Materials  
Science and Engineering<sup>b</sup>, The University of Texas at Austin,  
Austin, Texas 78712

**Abstract**

In order to produce chemically and environmentally stable forms of  $YBa_2Cu_3O_{7-\delta}$  superconductors, a series of cation substitution reactions were completed. It was found that the corrosion resistance increases with increasing  $y$  in  $Y_{1-y}Ca_yBa_{2-y}La_yCu_3O_{7-\delta}$ . The chemical degradation behavior in water for both bulk and thin film samples of  $Y_{1-y}Ca_yBa_{2-y}La_yCu_3O_{7-\delta}$  has been obtained along with similar data for the unsubstituted compound,  $YBa_2Cu_3O_{7-\delta}$ . The composition of  $Y_{0.6}Ca_{0.4}Ba_{1.6}La_{0.4}Cu_3O_{6.96}$  with a  $T_c = 80$  K was found to be at least 100 times more stable than  $YBa_2Cu_3O_{6.94}$ . The availability of these stable cuprate phases may facilitate more rapid commercialization of high- $T_c$  thin film structures and devices.

[accepted]

[Applied Physics Letter]

**IMPROVED CORROSION RESISTANCE OF CATION SUBSTITUTED  
YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-δ</sub>**

**Ji-Ping Zhou, Steven M. Savoy, Rung-Kuang Lo, Jianai Zhao,  
Mark Arendt, Y.T. Zhu,<sup>a)</sup> A. Manthiram<sup>a)</sup> and John T. McDevitt,\***

**Department of Chemistry and Biochemistry, The University of Texas  
at Austin,  
Austin, Texas 78712-1167**

**<sup>a)</sup>Center of Materials Science and Engineering, University of Texas  
at Austin, Austin, TX 78712-1063.**

**Abstract**

A cosubstitution of Ca<sup>2+</sup> for Y<sup>3+</sup> and La<sup>3+</sup> for Ba<sup>2+</sup> in YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-δ</sub> is found to improve the corrosion resistance of this high-T<sub>C</sub> superconductor. The reactivity characteristics of bulk and thin film samples of Y<sub>1-z</sub>Ca<sub>z</sub>Ba<sub>2-y</sub>La<sub>y</sub>Cu<sub>3</sub>O<sub>7-δ</sub> indicate that the corrosion resistance in water environments increases with increasing degree of cation substitution up to z = y = 0.4. The composition of Y<sub>0.6</sub>Ca<sub>0.4</sub>Ba<sub>1.6</sub>La<sub>0.4</sub>Cu<sub>3</sub>O<sub>6.96</sub> with a T<sub>C</sub> of 80 K is found to be at least 100 times more stable than YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6.94</sub>. Possible contributing factors that could be responsible for the marked improvement in the corrosion resistance of this high-T<sub>C</sub> phase are discussed.

[Physica C, Submitted]

**Enhanced Corrosion Resistance of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  Materials by  
Light Surface Fluorination**

**Ji-Ping Zhou<sup>a</sup>, Joel J. Kamp<sup>a</sup>, Mark Arendt<sup>a</sup>, David R. Riley<sup>a</sup>,  
K. Bussmann<sup>b</sup>, Richard J. Lagow<sup>a</sup> and John T. McDevitt<sup>a\*</sup>**

**<sup>a</sup>Department of Chemistry and Biochemistry, <sup>b</sup>Department of Physics,  
The University of Texas at Austin  
Austin, Texas 78712-1167**

**Abstract**

A light surface fluorination technique is exploited to alter the properties of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  ceramic samples. Unlike previous studies where more aggressive fluorination conditions were employed and reductions in the carrier density as well as the formation of amorphous degradation phases were noted, the mild fluorination conditions reported herein can be utilized to incorporate fluorine directly into the high- $T_c$  lattice without disruption of the basic structure. Consequently, more positive values for the copper and oxygen binding energies than seen in previous experiments by XPS are observed. Moreover, the special fluorination conditions identified here are shown to impart enhanced stability towards the adverse effects of water corrosion.

**Key words:**  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  superconductor, corrosion,  
protection, fluorination, and XPS